Fullerenes, Nanotubes and Carbon Nanostructures

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On the Radical Cation Spectra of Fullerenes and Fulleranes. Part 1: C\textsubscript{60}, C\textsubscript{70}, C\textsubscript{76}, C\textsubscript{78} and C\textsubscript{84}

Franco Cataldo \textsuperscript{a b}, Susana Iglesias-Groth \textsuperscript{c} & Arturo Manchado \textsuperscript{c d}

\textsuperscript{a} Istituto Nazionale di Astrofisica - Osservatorio Astrofisica di Catania, Catania, Italy
\textsuperscript{b} Actinium Chemical Research, Rome, Italy
\textsuperscript{c} Instituto de Astrofisica de Canarias, Tenerife, Spain
\textsuperscript{d} CSISC, Consejo Superior de Investigaciones Cientificas, Madrid, Spain

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On the Radical Cation Spectra of Fullerenes and Fulleranes. Part 1: C$_{60}$, C$_{70}$, C$_{76}$, C$_{78}$ and C$_{84}$

FRANCO CATALDO$^{1,2}$, SUSANA IGLESIAS-GROTH$^3$
AND ARTURO MANCHADO$^{3,4}$

$^1$Istituto Nazionale di Astrofisica – Osservatorio Astrofisica di Catania, Catania, Italy
$^2$Actinium Chemical Research, Rome, Italy
$^3$Instituto de Astrofisica de Canarias, Tenerife, Spain
$^4$CSISC, Consejo Superior de Investigaciones Cientificas, Madrid, Spain

The radical cation of the fullerene series C$_{60}$, C$_{70}$, C$_{76}$, C$_{78}$ and C$_{84}$ were generated in oleum (fuming sulphuric acid with 30% free SO$_3$) and analyzed by electronic absorption spectroscopy. A general agreement was found between the fullerences radical cation spectra generated in oleum and those described in the literature and produced in other conditions. An attempt to correlate the radical cation transition of C$_{60}$, C$_{70}$, C$_{76}$, C$_{78}$ and C$_{84}$ in oleum with their ionization potential was proposed.

Keywords Fullerenes, oleum, fuming sulphuric, radical cation, spectroscopy

Introduction

Cami et al. (1) were the first to report about the presence of C$_{60}$ and C$_{70}$ fullerenes in the young planetary nebula Tc1 using the Spitzer space telescope. More recently, fullerenes were found as a quite common component in a series of planetary nebulae checked with Spitzer (2). Garcia-Hernandez et al. (2) have estimated that the planetary nebulae analyzed, the amount of C$_{60}$ is $\approx 0.35\%$ the mass of the total carbon while Cami et al. (1) have reported a level of $\approx 1.5\%$ in Tc1. Furthermore, fullerenes were detected also in a couple of reflection nebulae in the interstellar medium (3). The detection of fullerenes in these astrophysical objects was interpreted as due to neutral C$_{60}$ and C$_{70}$ molecules (1). This was explained by admitting that the fullerenes were adsorbed on carbon dust. In fact, when fullerenes are adsorbed on a solid amorphous carbon phase, they will not be ionized by the stellar photons (1). Instead, the free fullerene molecules will be surely ionized at least into the corresponding radical cations. Some years ago, Ehrenfreund and Foing assigned to C$_{60}^{++}$ some spectral features observed in the diffuse interstellar bands (4).

Recently, we have dedicated great efforts on the study of fullerenes stability in space under the action of high energy radiation (5), on the study of the interaction between fullerenes and hydrogen or deuterium and in the infrared spectroscopy of fulleranes, the hydrogenated fullerenes (6–12) in view of their potential presence in planetary and/or protoplanetey nebulae (13). Furthermore, the photolysis and the thermal processing of fulleranes restore the fullerenes with the release of molecular hydrogen carbon dust and
other aromatic products; this back reaction is not fully reversible (8,9,12,14). For the qualitative detection of the fullerenes in space we have studied their infrared absorption band shift as function of the temperature (12,15), and for the quantitative determination of fullerene in space we have also measured the molar extinction coefficient and the integrated molar absorptivity of their infrared absorption bands at ambient temperature (16) and at absolute zero and high temperatures (17).

The present paper is dedicated to the measurement of the radical cation spectra of fullerene and fulleranes. In general, the radical cation spectra of aromatic molecules such as polycyclic aromatic hydrocarbons (PAHs) are characterized by strong electronic transitions; that is, the radical cation electronic transitions possess elevated molar extinction coefficients and are extremely sensitive to the polarity of the matrix where they are embedded (18), making these molecules easily searchable in space where they are ionized. For instance, naphthalene radical cation and other molecules have been identified by observational astronomy (19,20).

Experimental

Materials and equipment

Fullerenes C_{60} and C_{70} were high purity grades (99.95% and 99.0+%, respectively) from MTR Ltd. (USA). Fulleranes were synthesized as detailed elsewhere (6–12). A mixture of hydrogenated fullerenes was obtained from ABCR GmbH (Germany). Oleum (fuming sulphuric acid) with 30% free SO_{3} was from Merck (Germany).

The electronic absorption spectra of the radical cations were recorded on a Shimadzu UV2405 spectrometer in the range of 190–1100 nm (6.53–1.13 eV). Optical grade quartz UV cuvettes were used for recording the spectra.

Generation of the fullerene and fullerane radical cation

Warning! Oleum is an extremely corrosive and powerful oxidizing agent. The fumes released by oleum must not be breathed. Wear suitable protective gloves and goggles and always work under an an appropriate fume hood.

After a baseline correction (oleum vs. oleum), the spectra of the fullerene or fullerane radical cations were recorded by dissolving in oleum (3.5 ml) about <1 mg of the fullerene under study. Stirring with a glass stick was in most cases necessary to help in the fullerene or fullerane dissolution and homogeneization. The electronic spectra were recorded immediately after the PAHs dissolution at room temperature. In some cases the evolution of the electronic absorption spectrum with time was followed and studied as discussed in the results and discussion section.

Results and Discussion

Oleum as a medium for the synthesis of radical cations

The easiest way to generate a radical cation of an aromatic hydrocarbon consists in its dissolution in concentrated sulphuric acid (21). The acid serves as both solvent and oxidizing agent. However, oleum (fuming sulphuric acid) is a stronger oxidizing agent than concentrated sulphuric acid (22–28). Furthermore, oleum is a superacid (22). By definition, a superacid is any acid system that is stronger than 100% sulphuric acid, which means that its Hammet’s acidity function $H_0 \leq -12$. Oleum with 30% of SO_{3} has $H_0 = -13.76$
although also a value of about $-14.0$ has been reported (23). The oxidizing power
of oleum derives from the reduction of $SO_3$ when a suitable organic or inorganic sub-
strate is dissolved in the medium acting as a reducing agent. Elsewhere (18) we have
discussed in detail this aspect, reporting some experimental evidences. Molecules having
a ionization potential up to 10 eV are ionized to radical cations in oleum. Furthermore, the
resulting radical cations are stabilized by the high dielectric constant of the medium 110
(23). Therefore, oleum is an ideal medium to generate radical cations of organic substrates.
For instance, in 1995 Cataldo (29) succeeded in the synthesis of the radical cation of $C_{60}$
and $C_{70}$ fullerenes in oleum and in the medium composed by triflic acid and potassium
persulphate ($CF_3SO_3H + K_2S_2O_8$). Those results were confirmed later by other synthetic
approaches and analytical techniques (30,31).

$C_{60}$ radical cation in oleum: a revisitation

As reviewed by Reed et al. (31), the $C_{60}$ radical cation transition occurs in the near infrared
and is dependent also from the nature of the matrix were $C_{60}^+•$ is embedded. In a neon
matrix at 5K under irradiation the $C_{60}^+•$ transition occurs at about 965 nm, while in a Freon
matrix a 77K occurs at 980 nm (32). The $C_{60}^+•$ was found at 980 nm also in pulse radiolysis
experiments (33) but also in photoinduced electron transfer reaction in dichloromethane
and under photoionization conditions in Ar at 11K and by the action of $SbCl_5$ on $C_{60}$ in
chlorinated solvents (31). Only in strong superacid media such as “magic acid,” a mixture
of $FSO_3H$ and $SbCl_5$, is the $C_{60}^+•$ transition reported to occur at shorter wavelengths,
namely 818 nm or 742 nm, depending on the ratio $FSO_3H/SbCl_5$ (31). When $C_{60}$ it is
dissolved in $CF_3SO_3H$ containing the oxidizer potassium persulphate ($K_2S_2O_8$), the radical
cation band appears at 965 nm (29).

Concerning $C_{60}$ solutions in oleum, Cataldo (29) has reported a peak at 824 nm accom-
panied by another maximum at about 940 nm which develops on ageing. Miller et al. (34)
have interpreted the solutions of $C_{60}$ in oleum in terms of initial formation of the radical
cation reporting two absorption maxima at 824 and 929 nm, in line with Cataldo’s find-
ings, followed at later stages by a sultonation reaction. The electron spin resonance study of
fresh $C_{60}$ solutions in oleum has confirmed the radical cation nature of the specie formed
(35,36), and further minor species with $S = 1$ spin were also observed and tentatively
assigned to $C_{60}^{n+}$ ions, $n = 2, 4, \ldots$ in a triplet state (36).

More recent studies (37) have confirmed the sulphation reaction of $C_{60}$ in oleum, a
process which is strongly enhanced by the addition of certain oxidizing agents to oleum.
Furthermore, the interpretation of the evolution of the electron spin resonance spectra of
$C_{60}$ solutions in oleum (38) and the isolation of the reaction products suggest possible
dimerization and oligomerization reaction of the $C_{60}$ molecule involving the radical cation
intermediate step (39,40).

Figures 1 and 2 report the results of the dissolution of $C_{60}$ in oleum. The spectra
were recorded in thermostated cells at 50°C. As soon as the $C_{60}$ was added to oleum and
was dissolving, the spectra were recorded after defined intervals of time as illustrated in
Figures 1 and 2. Initially, only a relatively broad absorption band at about 824 nm can
be observed, and the solution becomes greenish. The band at 824 nm grows in intensity,
preumably as soon as more $C_{60}$ gets dissolved. Such absorption band is accompanied by
a shoulder at about 933 nm which becomes evident after 5 minutes from the beginning of
the dissolution of $C_{60}$. Initially the band at 933 nm grows in intensity together with the
band at 824 nm. However, after about 15 minutes after the experiment starts, the band at
824 nm stabilizes in intensity and remains stable for 26 minutes and then begins to decline
in intensity as shown in Figures 3 and 4. The overall trend of the two absorption bands can
Figure 1. Electronic absorption spectra of C_{60} in oleum. The spectra were taken (from bottom trace to top trace), respectively, at 0, 5, 9, 15, 18, 21 and 26 minutes after preparation at 50°C (color figure available online).

Figure 2. A detail of the electronic absorption spectra of C_{60} in oleum shown in Figure 1. The spectra were taken (from bottom trace to top trace), respectively, at 0, 5, 9, 15, 18, 21 and 26 minutes after preparation at 50°C. There is a steady growth of the band at 823.7 nm and of the shoulder at 931.5 nm. The arrows show the direction of growth of the absorption bands (color figure available online).
Figure 3. Electronic absorption spectra of C₆₀ in oleum. The spectra describe here a second stage where the band at 824 nm starts to decrease in intensity. The spectra were taken (from top trace to bottom trace), respectively, at 32, 52, 57, 75 and 95 minutes and 24 hours after preparation at 50°C (color figure available online).

Figure 4. A detail of the electronic absorption spectra of C₆₀ in oleum shown in Figure 3. The spectra were taken (from top trace to bottom trace), respectively, at 32, 52, 57, 75, 95 minutes and 24 hours after preparation at 50°C. There is a steady decrease in intensity of the band at about 824 nm as indicated by the arrow. The shoulder at about 933 nm at a certain point becomes the main peak and then it starts do decrease in intensity as well. In the later stages of this process also a shoulder at 1003 nm can be observed (color figure available online).
Figure 5. A complete account of the overall process reported in the four previous figures regarding the $C_{60}$ solution in oleum is summarized in this graph: initially the absorption band at about 821 nm grows more rapidly than the other band at 934 nm. Then the first band reaches a plateau while the latter band continues to grow. There is a third stage where the band at 821 nm decreases in intensity while the other band at 934 nm reaches a long plateau and finally decreases more slowly than the former band (color figure available online).

be followed in Figure 5. The decline of the intensity of the band at 824 nm is accompanied by a stable intensity of the band at 933 nm, which instead declines much more slowly and needs a long time to fade. The band at 933 nm is accompanied by a shoulder at about 1003 nm. Even after 24 hours from the beginning of the experiment, the band at 933 nm was still detectable and accompanied by two weaker bands at about 800 and 1003 nm (see Figures 3 and 4).

The original interpretation, that $C_{60}$ forms initially a charge-transfer complex with SO$_3$ or better, with S$_2$O$_6$ specie present in oleum (29) is substantiated by the recent studies on the sulfonation of fluoroalkenes with sulphur trioxide which calls for the formation of a $\pi$ complex between the olefin and sulphur trioxide as first reaction step (41). The olefin acts as donor and SO$_3$ as the $\pi$ charge acceptor. SO$_3$ is known as a strong Lewis acid. This idea of the formation of a charge transfer complex between the alkene and the SO$_3$ is substantiated both by theoretical calculations and experimental evidences (41). The same view was applied later to the interpretation of the sulfonation reaction mechanism of aromatic substrates (42): the latter substrate acts as a $\pi$ charge donor and SO$_3$ as an acceptor. Thus, even in the case of the sulfonation reaction of toluene with oleum, it was shown both by theoretical calculations and by an experimental evidence that the sulfonation reaction starts with the initial formation of a charge-transfer complex between toluene and SO$_3$ and when oleum was used, the active specie can be described by the SO$_3$ dimer S$_2$O$_6$ (42).

The evolution of the absorption bands can be interpreted in the following way: the band at 824 nm originates from the initial charge-transfer complex:

$$C_{60} + n\text{SO}_3 \rightarrow [C_{60} \pi \text{SO}_3]^n$$
Part of the $\pi$ electrons of C$_{60}$ is partially transferred to a series of SO$_3$ molecules, which act as acceptors and surround and in some way “solvate” the fullerene cage.

Such complex evolves into the formation of the true radical cation of C$_{60}^{+\cdot}$ with an absorption band at 933 nm line with the common knowledge that C$_{60}^{+\cdot}$ must absorb around 950 nm as discussed at the beginning of this section. Thus, the successive step from the $\pi$ complex can be described as:

$$[C_{60}^{\pi\rightarrow}(SO_3)_n] \rightarrow [C_{60}^{+\cdot}][\pi_n (SO_3)_n]^-$$

The radical cation is relatively stable and indeed its signature in the electronic absorption spectrum can be observed even after 24 hours from the beginning of the experiment. Of course the radical cation absorption peak at 933 nm declines slowly in intensity as time elapses because C$_{60}^{+\cdot}$ is consumed in multiple sulfonation reaction (34,36,37). Taking into account the high dilution of C$_{60}$ in the present experiment, it is reasonable to admit that the dimerization and the oligomerization reactions reported to occur in oleum (39,40) are just side reactions, even if the radical anions (and hence the radical cations) of C$_{60}$ dimer absorb in the same wavelength range of pure C$_{60}^{+\cdot}$ (43).

**C$_{70}$ radical cation in oleum**

Much less research work was dedicated to the less common fullerene C$_{70}$. In a earlier work on the dissolution of C$_{70}$ in oleum (29) a new absorption band attributed to C$_{70}^{+\cdot}$ was reported in reasonable agreement with CNDO/S calculations (32). At 5K in a neon matrix the spectrum of C$_{70}^{+\cdot}$ is characterized by a band between 714 and 806 nm (44). Figures 6 and 7 show the evolution of C$_{70}$ spectrum in oleum at 50°C. The solution is initially brown but turns green in color shortly thereafter. The bands at 329 and 452 nm observed in the early spectra recorded immediately after the dissolution of C$_{70}$ in oleum (Figures 6 and 7) are due to the neutral molecule (29). The new absorption band derived from the dissolution of C$_{70}$ in oleum and the presumable immediate ionization to C$_{70}^{+\cdot}$ occurs at 648 nm with a shoulder at 710 nm (Figures 6 and 7). Then the band at 648 nm grows in intensity as more and more C$_{70}$ get dissolved and ionized. Figure 8 is a plot of the increase of the intensity this absorption band assigned to C$_{70}^{+\cdot}$ as function of time. The plateau is reached after about $10^3$ s from the beginning of the dissolution of C$_{70}$; afterwards the intensity of the band at 648 nm remains stable for the next $5\times10^3$ s and more. However, in Figure 6 and especially in Figure 7 it is possible to appreciate a slow C$_{70}^{+\cdot}$ band shift toward shorter wavelengths as the time elapses, even when the intensity of the band was stabilized. This fact is illustrated in the graph of Figure 9. The shift of the C$_{70}^{+\cdot}$ is more pronounced in the first $10^3$ s from the beginning of the experiment to the first $10^3$ s passing from 648 nm to 640.5 nm (i.e., from 1.91 eV to 1.94 eV), which means that the radical cation electronic transition increases by 0.3 eV. For the following $5\times10^3$ s the C$_{70}^{+\cdot}$ remains stabilized at 1.94 eV. The growth of the intensity of the radical cation band at about 640 nm is accompanied by two side bands respectively 656 and 710 nm (see Fig. 8). Thus, the radical cation band of C$_{70}$ has a structure similar to the radical cation band of C$_{60}$ characterized at the later stages by a maximum at 934 nm and two shoulders at about 800 and 1003 nm. Only after $6\times10^3$ s the C$_{70}^{+\cdot}$ spectrum in oleum shows an additional weak and relatively broad band at 791 nm (Figure 8) such band was observed in aged solutions of C$_{70}$ in oleum (29).
Figure 6. Electronic absorption spectra of C$_{70}$ in oleum. The spectra were taken (from bottom trace to top trace), respectively, at about 0.5, 4, 7, 11, 20, 33, 54 and 98 min after preparation at 50°C. The arrow indicates the direction of the growth of the band at about 640 nm (color figure available online).

Figure 7. Electronic absorption spectra of C$_{70}$ in oleum. A detail of the previous spectrum 5. The spectra were taken (from bottom trace to top trace) respectively at about 0.5, 4, 7, 11, 20, 33, 54 and 98 min after preparation at 50°C (color figure available online).
Figure 8. Absorbance increase of the band at 640 nm assigned to C\textsubscript{70}\textsuperscript{+*} in oleum at 50°C.

Figure 9. Shift of the radical cation C\textsubscript{70} band toward shorter wavelengths as function of the ageing time in oleum at 50°C.

\textit{C\textsubscript{76} in oleum}

A few studies are available on the radical cation and radical anion of C\textsubscript{76} fullerene, which is not easily accessible as C\textsubscript{60} and C\textsubscript{70} (45–47). The radical cation C\textsubscript{76}{\textsuperscript{+*}} is characterized
Figure 10. Electronic absorption spectrum of C\textsubscript{76} in oleum (color figure available online).

by two absorption maxima at 780 and 980 nm (45,46). When it is dissolved in oleum, C\textsubscript{76} gives a brown solution which is characterized by two absorption maxima in the ultraviolet: 247 and 295 nm. Figure 10 shows the growth of the intensity of these two bands as the dissolution of C\textsubscript{76} proceeds in the superacid. No intense bands appear in the near infrared part of the spectrum as expected for the radical cation formation. However, an expansion of the spectrum of Figure 10 is shown in Figure 11, where it is possible to distinguish three broad absorption bands at 762, 914 and 1003 nm. The bands are weak because of the small amount C\textsubscript{76} available (<1 mg) which was dissolved in 3 ml of oleum. The tree bands observed in oleum occur at 1.63 eV, 1.36 eV and 1.24 eV respectively and are not far from the C\textsubscript{76}\textsuperscript{+•} transitions reported by other authors (45,46), respectively, at 1.59 eV and 1.27 eV considering the different reaction media where they were recorded.

\textit{C\textsubscript{78} and C\textsubscript{84} in oleum}

The higher homologues C\textsubscript{78} and C\textsubscript{84} are soluble in oleum. As reported for C\textsubscript{76}, only a small amount of C\textsubscript{78} and C\textsubscript{84} (<1 mg) were dissolved in 3 ml of oleum. As shown in Figure 12, the electronic absorption spectrum of C\textsubscript{78} in oleum shows two maxima at 247 and 291 nm in the ultraviolet, hence it is similar to that of C\textsubscript{76}. Figure 13 shows the visible and near infrared part of the absorption spectrum of C\textsubscript{78} in oleum. Because of the high dilution the electronic transitions in this part of the spectrum appear broad and weak. However, it is possible to distinguish the bands at 382 at 502 and at about 700 nm. Tentatively these two transitions could be assigned to C\textsubscript{78}\textsuperscript{+•}.

Figure 14 shows the spectrum of C\textsubscript{84} in oleum. Again the UV part of the spectrum is characterized by two peaks, respectively, at 250 and 298 nm. On the other hand, the spectrum in the visible and near infrared region is shown expanded in Figure 15. The spectrum shows three broad peaks at 393, 635 and 810 nm. The last two peaks may be assigned tentatively to C\textsubscript{84}\textsuperscript{+•}. Pulse radiolysis studies have shown that the radical cation of C\textsubscript{84} occurs at 920 nm (48).
Fullerenes ionization potential and radical cation transitions

Recently it was shown that there is a nice correlation between the ionization potential of a series of PAHs and the energy of their radical cation transition measured in oleum (18). Table 1 reports the ionization potential of a series of fullerenes taken from Ref. (49,50)
and a summary of the radical cation transitions observed in oleum and discussed in the preceding sections. It can be observed that the ionization potential of the fullerene series considered here is always around 7 eV with a deviation to 7.49 eV for C\textsubscript{60} fullerene. Since the ionization potential of graphite is at 4.39 eV (51), the ionization potential of higher
Figure 15. Expansion of the near infrared portion of the electronic absorption spectrum of C₈₄ in oleum shown in Figure 14. The arrow indicates the position of a weak and broad feature at 810 nm (color figure available online).

Table 1
Ionization potential and radical cation transition of fullerenes in oleum

<table>
<thead>
<tr>
<th>Fullerenes</th>
<th>First ionization potential (eV)</th>
<th>Fullerenes radical cation transitions (eV) in oleum</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆₀</td>
<td>7.49</td>
<td>1.50; 1.33</td>
</tr>
<tr>
<td>C₇₀</td>
<td>7.26</td>
<td>1.95; 1.57</td>
</tr>
<tr>
<td>C₇₆</td>
<td>7.06</td>
<td>1.63; 1.36; 1.24</td>
</tr>
<tr>
<td>C₇₈</td>
<td>6.96</td>
<td>2.47; 1.77</td>
</tr>
<tr>
<td>C₈₂</td>
<td>6.90</td>
<td></td>
</tr>
<tr>
<td>C₈₄</td>
<td>7.05</td>
<td>2.48; 1.96; 1.53</td>
</tr>
</tbody>
</table>

fullerenes is at least 2.61 eV higher than graphite. On the other hand, the lowest energy radical cation transition observed in oleum for the complete fullerene series is comprised in the relatively narrow range comprised between 1.24 and 1.77 eV. In the case of PAHs it has been found a simple correlation between the first ionization potential \( I_{P1} \) and their radical cation transition \( (h\nu)_{PAHs} \) measured in oleum (18):

\[
I_{P1} = 1.30 (h\nu)_{PAHs} + 4.39
\]  

(1)

where the constant 4.39 eV is the working function of graphite (51). In the case of fullerenes equation (1) should be approximated very roughly to:

\[
I_{P1} \approx 1.7 (h\nu)_{Fullerenes} + 4.39
\]  

(2)
Equation (2) should permit to link the longest wavelength radical cation transition as measured in oleum with the ionization potential of the fullerenes.

Conclusions

Oleum (fuming sulphuric acid with 30% free SO₃) is an ideal medium to produce quickly the radical cation of the complete fullerene series C₆₀, C₇₀, C₇₆, C₇₈ and C₈₄. The electronic absorption spectra of the fullerenes series radical cation generated in oleum were recognized using literature data as reference. Furthermore, it was shown that the fullerene radical cation transition is linked to the ionization potential of the fullerene series in an equation analogous to that used to connect the radical cation transition of PAHs with their ionization potential (18).

The knowledge of the radical cation transition of fullerenes could be useful in the search of fullerenes in space especially in places where the fullerene is not in neutral form but is ionized by high energy radiation.

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